



2-Nitrophenylpyruvic acid as a cathode material in a magnesium/zinc-based primary battery

R. RENUKA

Central Electrochemical Research Institute, Madras Unit, CSIR Madras Complex, Chennai 600 113, India

Received 27 April 1999; accepted in revised form 12 October 1999

Key words: 2-nitrophenylpyruvic acid, 2-nitrophenylpyruvic acid cathode, organic battery

Abstract

The efficiency of 2-nitrophenylpyruvic acid as a cathode material in a magnesium/zinc based primary battery is examined. The discharge performance of the cell is investigated under different parametric variations such as temperature, nature of electrolyte, current drain and zeolite modification. A 7e reduction seems to be responsible for the electrochemical reaction causing the reduction of 2-nitrophenylpyruvic acid to an indole intermediate which is oxidatively cleaved to form anthranilic acid as the end-of-discharge product. Participation of oxygen in the reduction process is indicated. The discharge capacity is 1.03 Ah g^{-1} , the highest value ever observed in organic batteries.

1. Introduction

The use of organic compounds as cathode materials in batteries is well known [1]. Nitro compounds offer high coulombic efficiency because the reduction of a single nitro group to the amino group involves addition of six electrons. Several nitro compounds such as *m*-dinitrobenzene [1, 2], alkyl substituted dinitrobenzenes [3], *p*-nitrotoluene [4, 5] 1-nitronaphthalene [6], *p*-nitrophenol [7], *p*-nitroaniline [8], 2- β -dinitrostyrene [9], picric acid and trinitrostilbene [10] have been investigated for their cathode performance in zinc and magnesium based cells. In the present study, the performance of 2-nitrophenylpyruvic acid as a cathode material in a magnesium/zinc based primary cell is reported. The significance of using 2-nitrophenylpyruvic acid is that it presents a unique combination of a nitro group, and carbonyl/carboxylic moieties. The nuances in the behaviour of the nitro group under the influences of neighbouring groups become very important in the selection of potential nitro compounds for battery applications. Since zeolite modification has been shown [9] to improve the efficiency of organic cathodes, the same effect has also been studied with 2-nitrophenylpyruvic acid and the results are also discussed.

2. Experimental details

Unless otherwise specified, all chemicals were Merck extrapure products. 2-nitrophenylpyruvic acid (m.p. 120°C) was prepared by acid catalysed condensation of 2-nitrobenzaldehyde with aceturic acid [11].

Double distilled water was used in preparing the electrolyte solutions. The zeolite used was a β -zeolite (Union Catalysts India).

Magnesium alloy AZ31 sheet 0.0015 m thick and zinc sheet (99.9% purity) 0.002 m thick were used for the magnesium and zinc anodes, respectively. Zeolite modification of 2-nitrophenylpyruvic acid was made by continuously stirring a blend of 10:1 zeolite: 2-nitrophenylpyruvic acid in benzene for 10 h. The solid was then filtered, washed and dried.

The cathode plate was made by mounting a uniform mixture of PTFE binder (0.2 ml), zeolite modified or unmodified 2-nitrophenylpyruvic acid and colloidal graphite on a nickel plated mild steel or copper mesh of dimensions $0.04 \text{ m} \times 0.025 \text{ m} \times 0.002 \text{ m}$. The material was then compacted using a hydraulic press.

In the cell (Figure 1), a cathode was positioned between two anodes. Direct contact of the cathode with anodes was prevented by pasting a pair of thin PVC wires on to the inner side of the zinc sheets.

The electrolyte consisted of ZnCl_2 (28%) and NH_4Cl (23%) in 100 ml water for zinc cells and 2 M MgCl_2 or 2 M MgBr_2 or 2 M $\text{Mg}(\text{ClO}_4)_2$ for magnesium cells. Unless otherwise specified the battery discharge was made at a constant current drain of 100 mA. Separation of the electrode reaction product from the zeolite matrix was done using chloroform.

Cyclic voltammograms were recorded using a PAR instrument (potentiostat/galvanostat model 163) a current-to-voltage convertor (model 176) a universal programmer (model 175) and a model RE 008 XY recorder. A platinum foil of large area was used as the auxiliary electrode while a saturated calomel electrode was used

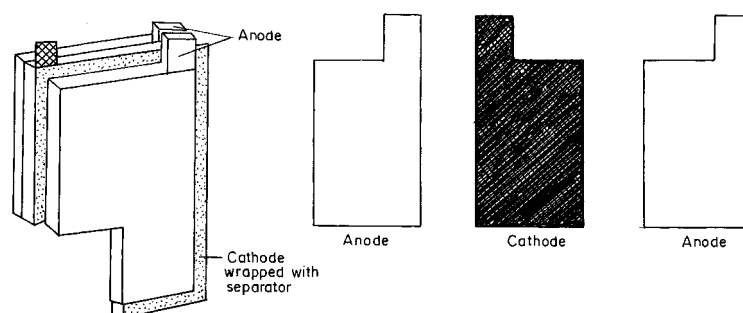


Fig. 1. Anode-Cathode arrangement.

as the reference. The solutions were deaerated by passing oxygen-free nitrogen through them. The cyclic voltammograms of the chloroform extract of the cathode mix were registered using HMDE (Metrohm) and Walpole acetate buffer, pH 3.6, containing 0.1 M KNO_3 .

3. Results and discussion

3.1. General discharge performance

The discharge curves of a 2-nitrophenylpyruvic acid battery in magnesium and zinc based cells are shown in Figures 2-4. Neither high nor low compaction pressure was suitable for the performance of the cells. An optimum pressure of 34 MPa (Figure 2) applied over the cathode area and 80 wt% colloidal graphite (Figure 3) was adequate for good performance in both zinc and magnesium based cells. It is an established fact that neither low pressure nor high pressure of compaction is suitable for battery plate fabrication. This is because while low pressure does not effect good adhesion of the active material with the current collector,

high pressure reduces the porosity of the plate. For magnesium cells, magnesium perchlorate electrolyte was superior to magnesium chloride and bromide (Figure 4). A small amount of (0.1 wt%) V_2O_5 increased the ampère-hour capacity by about 7%. For the current collector, copper mesh was superior to nickel plated mild steel (Table 1).

Figure 5 presents a comparison of the zinc-2-nitrophenylpyruvic acid cell with that of conventional manganese dioxide cells coupled with magnesium or zinc. Although the cell voltage of the 2-nitrophenylpyruvic acid cell is not as high as that of the manganese dioxide based cells, the former gives almost a flat discharge.

The effect of temperature variation on discharge performance is shown in Figure 6. As temperature decreases, there is a decrease in the capacity of the zinc based cells together with a slight decrease in the cell voltage. At 0 °C, the total output of the cell is only 60% of the output at room temperature. In contrast, magnesium cells exhibit excellent low temperature performance, resulting from the well established heat generating corrosion of the magnesium anode [12].

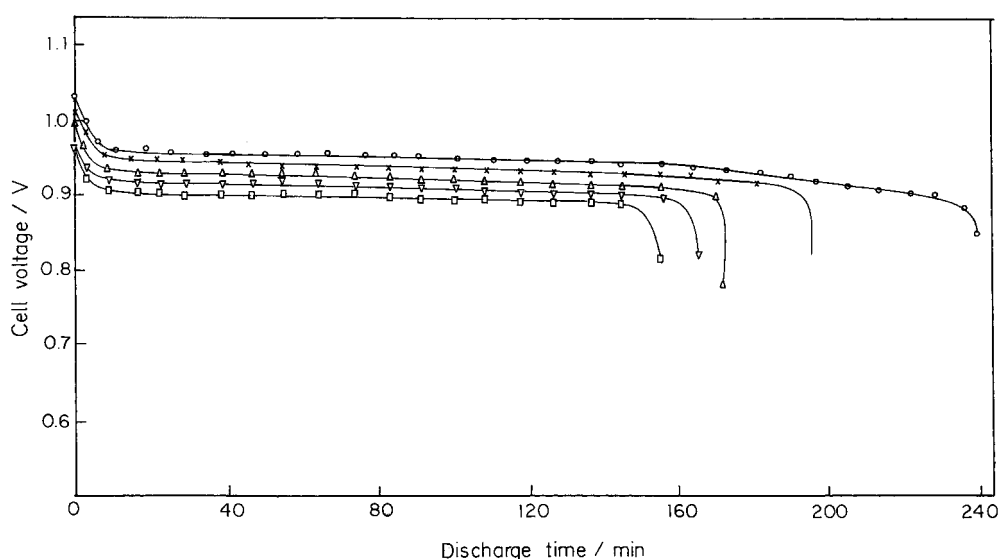


Fig. 2. Effect of compaction pressure on the discharge performance of $\text{Mg}/\text{Mg}(\text{ClO}_4)_2$ -2-nitrophenylpyruvic acid (0.40 g) cell. Colloidal graphite: 80 wt%; constant current drain: 100 mA. Pressure: (○) 34, (×) 45, (△) 27, (▽) 13 and (□) 7 kg MPa.

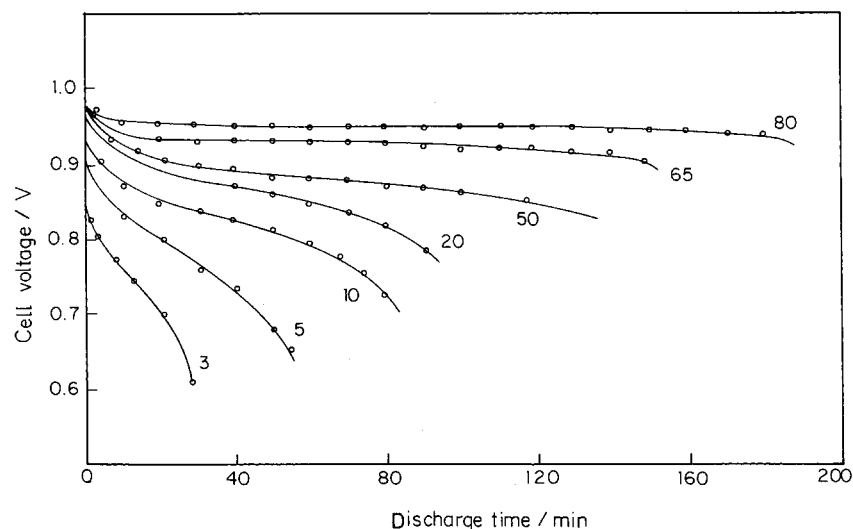


Fig. 3. Effect of colloidal graphite content on the discharge performance of Mg/Mg(ClO₄)₂-2-nitrophenylpyruvic acid (0.285 g) cell. Compaction pressure 3.4 kg m⁻²; constant current drain 100 mA.

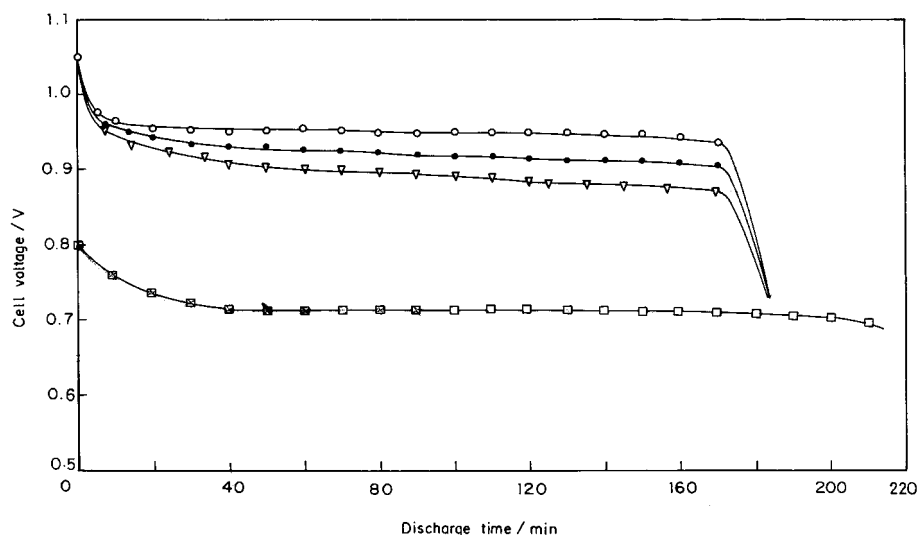


Fig. 4. Discharge curves of zinc (or magnesium)-2-nitrophenylpyruvic acid (0.285 g) cell. Key: (○) Mg(ClO₄)₂/Mg; (●) MgCl₂/Mg; (▽) MgBr₂/Mg; (□) ZnCl₂-NH₄Cl/Zn.

Table 1. Capacity of 2-nitrophenylpyruvic acid cathode

Anode	Cathode current collector	Electrolyte	V ₂ O ₅ catalyst	Zeolite modification	Capacity/Ah g ⁻¹
Mg	Cu mesh	2 M Mg(ClO ₄) ₂	—	—	0.85
Mg	Cu mesh	2 M MgCl ₂	—	—	0.85
Mg	Cu mesh	2 M MgBr ₂	—	—	0.85
Mg	Cu mesh	2 M Mg(ClO ₄) ₂	0.1 wt %	—	0.90
Mg	Cu mesh	2 M Mg(ClO ₄) ₂	—	yes	1.01
Zn	Cu mesh	ZnCl ₂ /NH ₄ Cl	—	—	1.03
Zn	Cu mesh	ZnCl ₂ /NH ₄ Cl	—	—	1.09
Zn	Cu mesh	ZnCl ₂ /NH ₄ Cl	0.1 wt %	yes	1.19
Mg	Ni-plated mild steel	2 M Mg(ClO ₄) ₂	—	—	0.62
Zn	Ni-plated mild steel	ZnCl ₂ /NH ₄ Cl	—	—	0.79

3.2. Zeolite modification of 2-nitrophenylpyruvic acid

Zeolites are attractive materials for electrode modification because they are ion-exchange materials, they have molecular sieving properties and are potential catalysts.

Several examples of the application of zeolites and its analogues in electrochemical phenomena can be quoted [13–32]. Recently, we reported the zeolite modification of chloranil and embelin battery cathodes [33, 34] as a clean technological route. The discharge curves of the

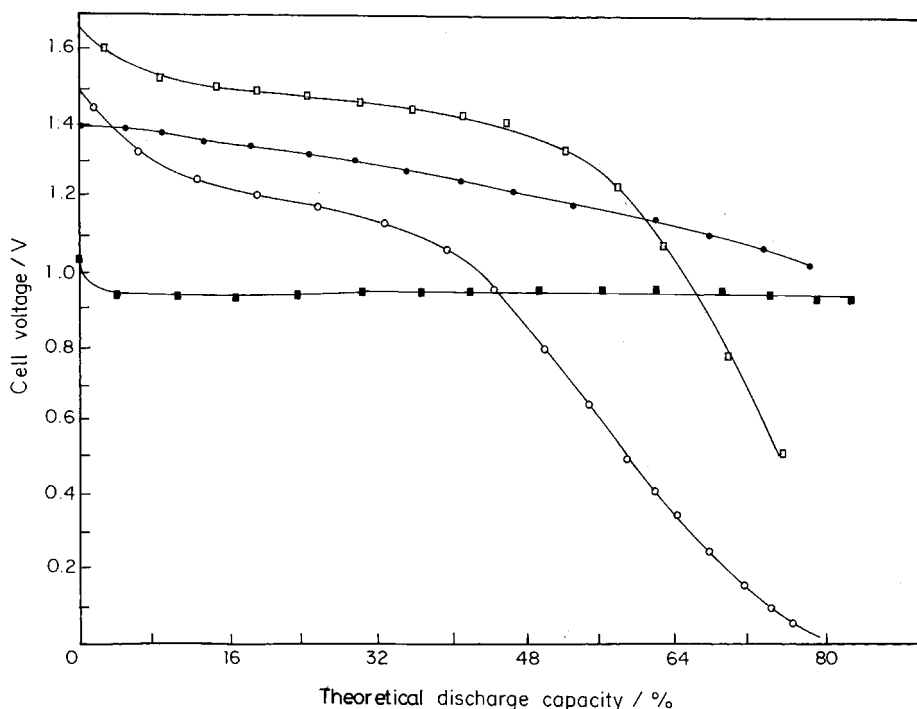


Fig. 5. A comparison of 2-nitrophenylpyruvic acid cell with that of conventional cells of magnesium or zinc. Key: (□) Mg/Mg(ClO₄)₂/MnO₂; (●) Zn/KOH/MnO₂; (○) Zn/NH₄Cl/MnO₂; (■) Mg/2nppA/Mg(ClO₄)₂.

battery with and without zeolite modification are shown in Figure 7. Zeolite modification brings about a remarkable improvement in the Ah capacity of the 2-nitrophenylpyruvic acid cell. The mechanism of participation of zeolites in organic reactions is now well understood. The participation is through (a) stabilization of short-lived radicals (b) Bronsted acidity and (c) product selectivity and the mode of assistance being dependent on the Si/Al ratio.

The variation of cell voltage with current density is shown in Figure 8. The slope of such a plot can be taken as a measure of the gross internal resistance of the cell. A comparison of the internal resistance value for a cell with and without zeolite shows that the introduction of zeolite increases the internal resistance of the cell. This is, however, compensated by the increased ampère-hour capacity emanating from the assistance of large pore size β -zeolite enabling a more uniform distribution of colloidal graphite, facile access of the electrolyte and prevention of gas locking in the cathode.

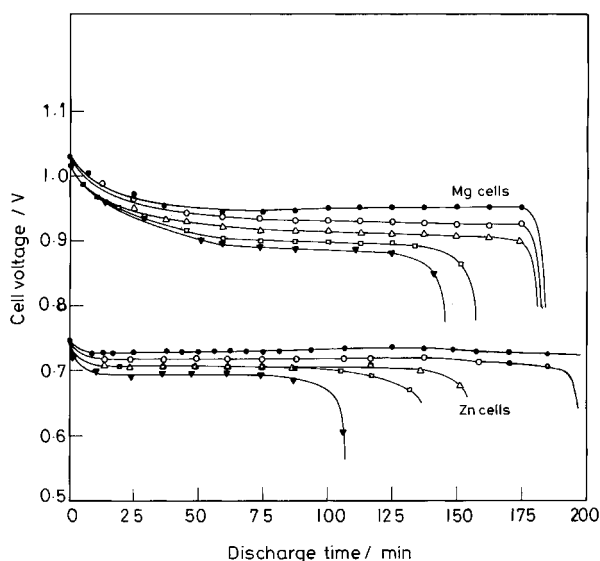


Fig. 6. Effect of temperature variation on discharge performance of zinc (or magnesium)-2-nitrophenylpyruvic acid (0.285 g) cell. Temperature: (●) 315, (○) 308, (△) 300, (□) 288 and (▼) 273 K.

3.3. Cyclic voltammetry

The cyclic voltammograms of the cathode active material on a mercury electrode (only the organic component removed from a battery at different stages during discharge) are shown in Figure 9. The irreversible couple corresponds to the reduction of the nitro group [35]. In general, the polarographic reduction of a polynitro aromatic compound proceeds in a stepwise manner, and the first step corresponds to a four electron change. This has been interpreted as corresponding to the reduction of one of the nitro groups to a hydroxylamino group. As the discharge of 2-nitrophenylpyruvic acid progressed, a reduction in the peak current of the cyclic voltammogram is observed. This observation indicates a reduction in the quantity of the starting material, namely, 2-nitrophenylpyruvic acid. A detailed study of polarographic reduction of 2-nitrophenylpyruvic acid is being separately carried out and will be published subsequently.

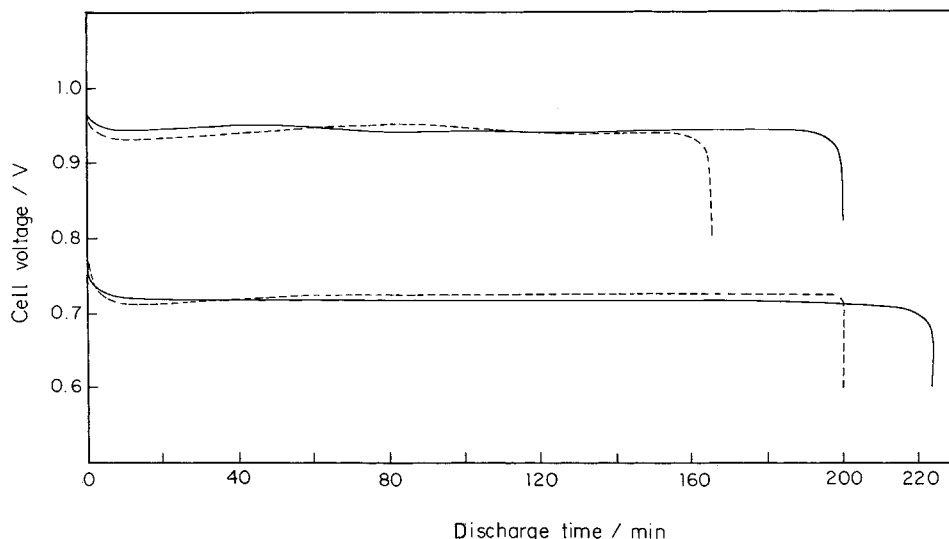


Fig. 7. Effect of zeolite modification on the discharge performance of Zn/ZnCl₂-NH₄Cl or Mg/Mg(ClO₄)₂-2-nitrophenylpyruvic acid (0.285 g) cell. Colloidal graphite 80 wt %; compaction pressure 3.4 kg m⁻². Constant current drain 100 mA. Key: (—) with zeolite; (---) without zeolite.

3.4. Spectral analysis

The infrared (IR) spectrum of the organic compound isolated from the end-of-discharge product (copper mesh as the current collector and Zn as anode) is shown in Figure 10, curve (b). The spectral pattern is completely different from that of 2-nitrophenylpyruvic acid (Figure 10, curve (a)). It can be seen that the absorptions characteristic [36] of the nitro group (1550, 1420, 880 cm⁻¹) are absent in the spectrum of the product. On the other hand, frequencies characteristic of COOH (1760, 1440, 1320 cm⁻¹) and NH₂ (3300, 1580, 1250 cm⁻¹) functionalities are seen.

Figure 11 presents the ultraviolet (UV) spectral analysis of the discharge product at different stages during the discharge. As discharge proceeds, the intensity of the absorption owing to 2-nitrophenylpyruvic acid ($\lambda_{\text{max}} =$

320 nm, 392 nm) decreases whereas a new spectrum develops with three maximas at 288 nm, 279 nm and 272 nm; UV spectral literature points out that a spectrum with three distinct maximas at 286 nm, 278 nm and 270 nm is characteristic of indole chromophore. The UV spectrum of an authentic sample of indole is also included in Figure 11 for comparison. The formation of indole from 2-nitrophenylpyruvic acid may be accounted for by the following electroreductive cyclization. (Scheme 1) involving a six electron transfer from the anode to the cathode [37].

As discharge proceeds further beyond 50%, the absorptions owing to indole chromophore decrease while a new absorption is emerging at 244 nm (Figure 11). In the light of the IR data, the new absorption may be attributed to anthranilic acid. The Ah capacity of a zinc based cell with copper mesh as the current collector was 1.03 Ah per gram of cathode material (without

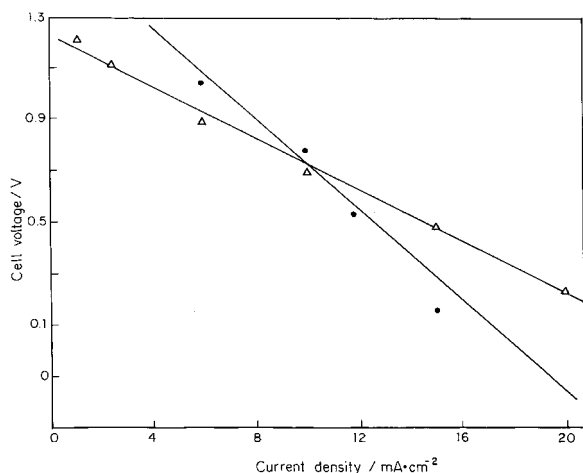


Fig. 8. Dependence of cell voltage on current density in Mg/2 M Mg(ClO₄)₂-2-nitrophenylpyruvic acid cell, with and without zeolite modification. Slope: (Δ) 59.3 mΩ cm² (without zeolite); (●) 84.7 mΩ cm² (with zeolite).

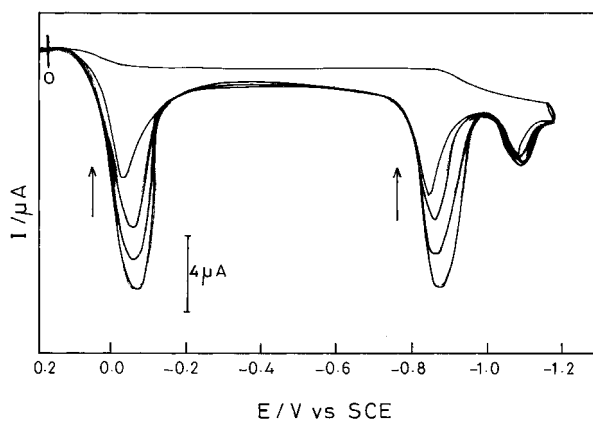


Fig. 9. Cyclic voltammograms of 2-nitrophenylpyruvic acid at regular intervals during discharge. 1-4 represent respectively 10-40% discharge. Chloroform extract of the cathode material was concentrated to 100 ml. 1 ml of this extract was made up to 250 ml in Walpole acetate buffer pH 3.6 containing 0.1 M KNO₃.

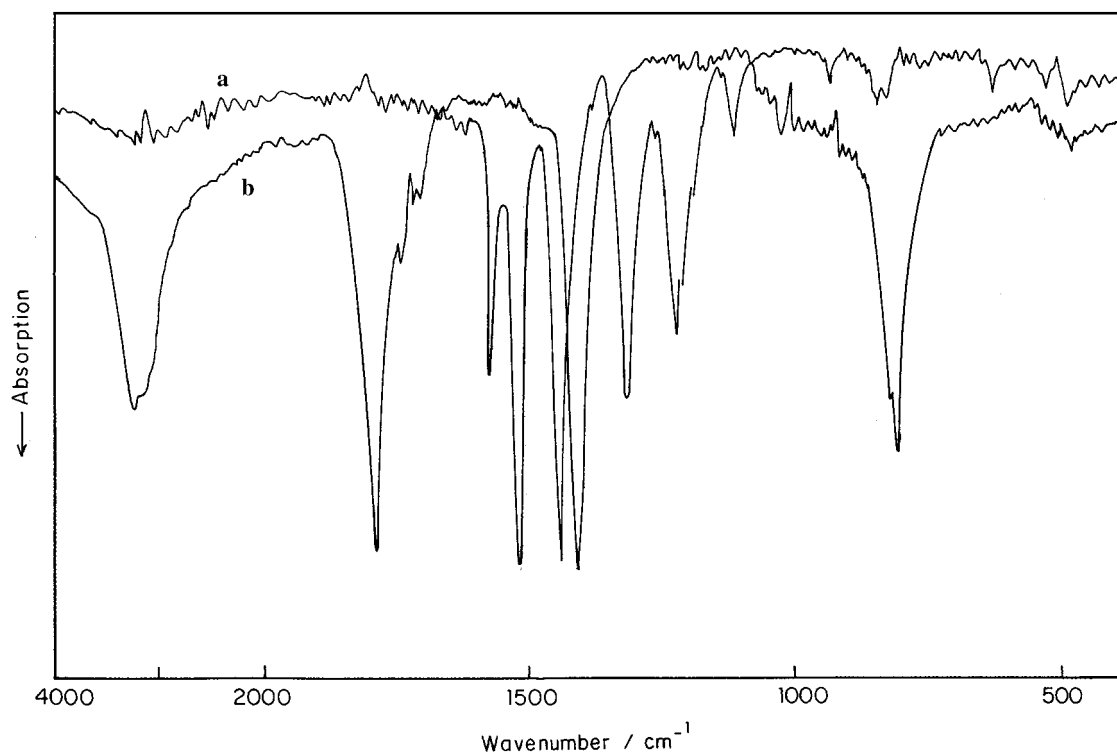


Fig. 10. IR spectrum of (a) 2-nitrophenylpyruvic acid (b) end-of-discharge product.

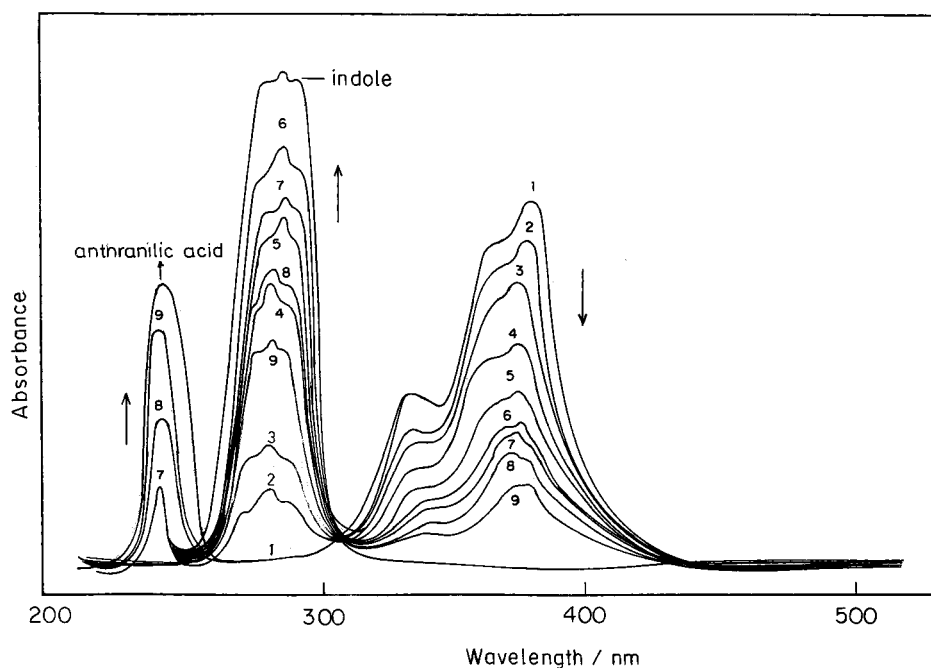
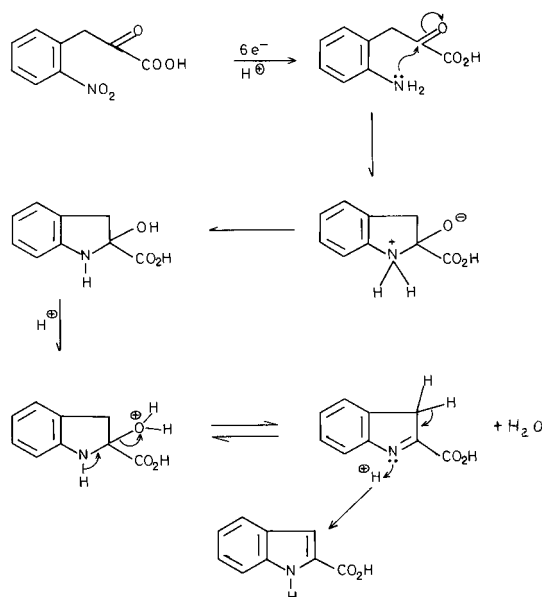


Fig. 11. UV spectra of 2-nitrophenylpyruvic acid at regular intervals during discharge. 1–4 represent respectively 10–40% discharge. Chloroform extract of the cathode material was concentrated to 100 ml. 1 ml of this extract was made up to 250 ml in chloroform. (Reference cell contains chloroform.)

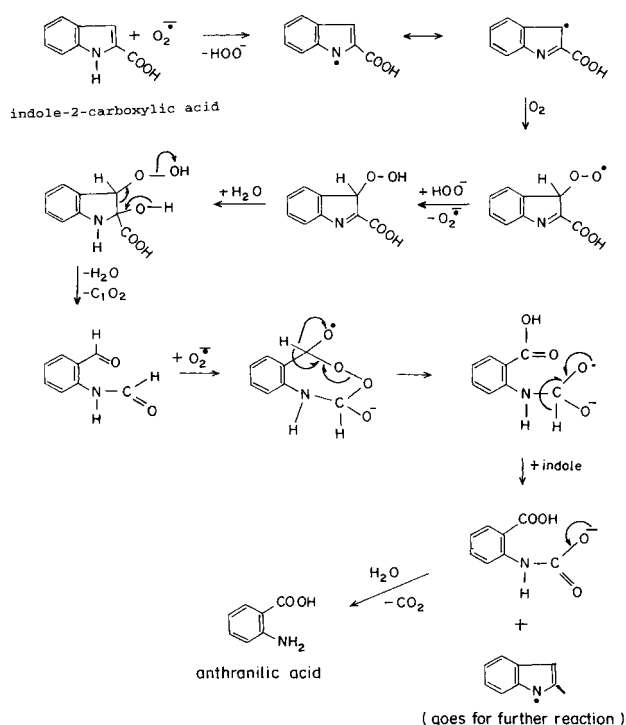
zeolite modification) which amounts to more than the theoretical coulombic efficiency (i.e., 0.73 Ah g^{-1} for 100% conversion) of the active material for the 6e reduction of the nitro group indicating participation of an extraneous depolarizer in the cell discharge.

In the search for possible additional depolarizer and reaction modes, a possibility that emerges is the participation of atmospheric oxygen. This proposition is strengthened by the fact that indole derivatives [38] are acted upon by oxygen and oxygen species leading to the



Scheme 1.

cleavage of the pyrrole moiety [39–41]. Under such conditions, the parent indole is converted into anthranilic acid. Further superoxide anion, $O_2^{\cdot -}$ is frequently invoked in the oxidation of indoles in electrochemical [39], biochemical [40] and photochemical [41] reactions. With this background, a 1e reduction of molecular oxygen can be proposed to take place at the cathode to generate $O_2^{\cdot -}$ which supplements the discharge extending the current out put (Scheme 2). Thus, as has been proposed for 2- β -dinitrostyrene cathode [9], a 7e reaction may be postulated for the discharge of 2-nitrophenylpyruvic



Scheme 2.

acid. However, a 7e reaction still does not account for 1.03 Ah per gram. While air-depolarization involving the discharge of atmosphere oxygen may compete with the discharge of 2-nitrophenylpyruvic acid, it is of interest to examine whether 2-nitrophenylpyruvic acid undergoes reduction involving the carbonyl group although eventually leading to anthranilic acid. If the carbonyl group were to participate in the cell discharge it could account for an additional 2e. However, a detailed analysis is necessary to ascertain the involvement or not of the carbonyl group. The present IR analysis of the end-of-discharge product has not been very helpful in discerning the fate of the carbonyl group during the discharge. Future studies could concentrate on the use of fast sweep spectroelectrochemical methods for this purpose.

4. Conclusion

2-nitrophenylpyruvic acid is found to be an efficient cathode material for primary batteries. The discharge is flat and the reduction (7e) proceeds through an electro-reductive cyclization to indole which is acted upon by oxygen to form anthranilic acid. The participation of oxygen in the electrode discharge is a remarkable phenomenon that could lead to defining 2-nitrophenylpyruvic acid as an 'air breathing' electrode.

Acknowledgements

The author thanks Union Catalysts, India, and Prof. C.N. Pillai, Emeritus Scientist, CECRI Madras Unit and Prof. B. Viswanathan, Chemistry Department, IIT Madras, Chennai for their help in the present work. Financial support to the work from Council of Scientific and Industrial Research, New Delhi, India (Vide EMR II/80(0027)/97) is gratefully acknowledged.

References

1. R. Glicksman and C.K. Morehouse, *J. Electrochem. Soc.* **105** (1958) 295.
2. A. Sivashanmugam, G. Kumar and N. Muniyandi, *Ext. Abstr. Proc. Meet. The Electrochem. Soc.*, Honolulu HI, USA (16–21 May 1993), Abstr. 101, p. 151.
3. K. Sivasamy, S. Rajeswari and K. Dakshinamurthi, *J. Power Sources* **25** (1989) 295.
4. G. Kumar, A. Sivashanmugam and N. Muniyandi, *J. Power Sources* **39** (1992) 121.
5. A.L. Endrey and T.A. Reilly, Proceedings of the 22nd Annual Power Sources Conference (May 1989), p. 51.
6. R. Thirunakaran, S. Vasudevan, A. Sivashanmugam, G. Kumar and N. Muniyandi, *J. Power Sources* **58** (1996) 213.
7. G. Kumar, A. Sivashanmugam and R. Sridharan, *J. Electrochem. Soc.* **140** (1993) 3087.
8. G. Kumar, A. Sivashanmugam and N. Muniyandi, *J. Appl Electrochem.* **23** (1993) 265.
9. R. Renuka, *J. Power Sources*, 1999, in press.
10. R. Renuka, S. Saravanan and P.C. Srinivasan, Proceedings of the 6th International Symposium on 'Advances in Electrochemical

- Science & Technology', SAEST (26–28 Nov. 1998), Chennai, India, in press.
11. Van der Lee, *Rec. Trav. Chem.* **44** (1925) 1089.
 12. J.P. Harivel, J. Doll, R.S. Cattle and R.J. Gale, in D.H. Collins (Ed.), *Power Sources*, 4, Oriel Press, Newcastle upon Tyne, pp. 51–61.
 13. Furukawa Battery Co., Ltd., *Jpn. Patent* 83 122 63 (1983); *Chem. Abstr.* **99** (1983) 25450g.
 14. T. Inoue, K. Kobayashi and K. Matsuo, *Jpn. Patent* 87 193 060 (1987); *Chem. Abstr.* **108** (1988) 8802g.
 15. A. Moor, *Ger. Patent* 1 302 003 (1969); *Chem. Abstr.* **73** (1970) 126473g.
 16. M. Crucena, E. Popovici and A. Vasile, *Rom. Patent* RO 78 511 (1982); *Chem. Abstr.* **99** (1983) 125685c.
 17. K. Miwa, K. Iwayama and H. Fukui, *Jpn. Patent* 87 241 265 (1987); *Chem. Abstr.* **108** (1988) 24622d.
 18. Debra R. Rolison, *Chem. Rev.* **90** (1990) 867.
 19. D.R. Rolison, C.A. Bessel, M.D. Baker, C. Seneratne and J. Zhang, *J. Phys. Chem.* **100** (1996) 8610.
 20. T. Bein and P. Enzel, *Angew. Chem. Int. Ed. (Engl)* **28** (1989) 1692.
 21. T. Bein and P. Enzel, *Synth. Metals* **29** (1989) E163; *J. Phys. Chem.* **93** (1989) 6270.
 22. A.J. Bard and T.E. Mallou, in 'Molecular Design of Electrode Surfaces', edited by R.W. Murray, cited in [15].
 23. C. Johansson, L. Risinger, L. Fallth and L. Huy, *Sci. Inst.* **49** (1980) 47.
 24. R.P. Townsend, *Pure Appl. Chem.* **58** (1986) 1359.
 25. J. Sarradin, J. Louvet, R. Mersina and J. Perchon, *Zeolites* **4** (1984) 157.
 26. D.W. Breck, 'Zeolite Molecular Sieves: Structure, Chemistry & Use' (Wiley-Interscience, New York, 1974).
 27. W.M. Meier and D.H. Olsen, 'Atlas of Zeolite Structure Types' (Juris Press, Zurich, 1978).
 28. J.A. Jacobs, 'Carboniogenic Activity of Zeolites' (Elsevier, Amsterdam, 1977).
 29. J.B. Peri, in 'Catalysis: Science and Technology' edited by J.R. Anderson and R.M. Boudart (Springer-Verlag, Berlin, 1984), p. 191.
 30. W.F. Holderich and H. Van Bekkum, *Stud. Surf. Sci. Catal.* **58** (1991) 631.
 31. V. Ganesan and R. Ramaraj, *Langmuir* **14** (1998) 2497.
 32. K. Pitchumani, Joy Abraham, Prevost Nicolette and V. Ramamurthy, *Chem. Commun.* (1997) 127.
 33. R. Renuka and D. Kalaiselvi, *J. Chem. Technol. Biotechnol.* 1999, in press.
 34. R. Renuka and D. Kalaiselvi, *J. Appl. Electrochem.* **29** (1999) 797.
 35. J. Heyrovsky and P. Zuman, 'Practical Polarography' (Academic Press, New York, 1950).
 36. R.N. Jones and C. Sandorfy, The Application of Molecular Structure in 'Technique of Organic Chemistry' Vol. IX, edited by A. Weissberger (Interscience, London, 1956), p. 463.
 37. C. Sharad Mishra and A. Ram Mishra, *J. Electrochem. Soc. India* **39** (1990) 51.
 38. A. Weissberger, (Ed.), 'Heterocyclic Compounds with Indole and Carbazole Systems' (Wiley Interscience, New York, 1954).
 39. A. Renuka and K. Shakuntala, *Bioelectrochem. Bioenergetics* **19** (1988) 161.
 40. R.J.P. Williams and J.J.R.F. Da Silva, in 'New Trends in Bio-Inorganic Chemistry' edited by R.J.P. Williams and J.J.R.F. Da Silva (Academic Press, New York, 1978) Chapter 5.
 41. D.M. Daniel and Wayner, *Bioelectrochem. Bioenergetics* **18** (1987) 219.